

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>7</sup> :</b> <b>C09K 11/06, H05B 33/14, H01B 1/12</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 00/06665</b> <b>(43) International Publication Date:</b> 10 February 2000 (10.02.00)
<b>(21) International Application Number:</b> PCT/US99/16834 <b>(22) International Filing Date:</b> 23 July 1999 (23.07.99)  <b>(30) Priority Data:</b> 09/123,271                      28 July 1998 (28.07.98)                      US  <b>(71) Applicant:</b> THE DOW CHEMICAL COMPANY [US/US]; 2030 Down Center, Midland, MI 48674 (US).  <b>(72) Inventors:</b> BERNIUS, Mark, T.; 401 Mayfield Lane, Midland, MI 48640 (US). WOO, Edmund, P.; 300 Mayfield Lane, Midland, MI 48640 (US). WUJKOWSKI, Lisa, L.; 4330 Midland Road, Saginaw, MI 48603-9666 (US). INBASEKARAN, Michael; 2614 Walden Woods Court, Midland, MI 48640 (US).  <b>(74) Agent:</b> ZERULL, Susan, M.; The Dow Chemical Company, Patent Dept., P.O. Box 1967, Midland, MI 48641-1967 (US).		<b>(81) Designated States:</b> CA, CN, JP, KR, SG, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> ORGANIC ELECTROLUMINESCENT DEVICES		
<b>(57) Abstract</b>  An electroluminescent (EL) device containing a light-emitting organic film, arranged between an anode material and a cathode material such that under an applied voltage, the device is forward biased and holes are injected from the anode material into the organic film adjacent to the anode material and electrons are injected from the cathode material into the organic film adjacent to the cathode material, resulting in light emission from the light-emitting organic film; wherein the device also contains a solution-processed film of a blend of an acid-functional non-conductive polymer and a conductive polymer positioned between the anode material and the light-emitting organic film, wherein the weight ratio of non-conducting polymer to conducting polymer is at least 0.75:1.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon	KR	Republic of Korea	PL	Poland		
CN	China	KZ	Kazakhstan	PT	Portugal		
CU	Cuba	LC	Saint Lucia	RO	Romania		
CZ	Czech Republic	LI	Liechtenstein	RU	Russian Federation		
DE	Germany	LK	Sri Lanka	SD	Sudan		
DK	Denmark	LR	Liberia	SE	Sweden		
EE	Estonia			SG	Singapore		

## ORGANIC ELECTROLUMINESCENT DEVICES

This invention relates to organic-containing electroluminescent devices and, more particularly, to such devices which contain an organic electroluminescent layer and an organic hole-transport layer.

5           An organic electroluminescent device typically consists of an organic film sandwiched between an anode and a cathode, such that when a positive bias is applied to the device, holes are injected into the organic film from the anode and electrons are injected into the organic film from the cathode. The combination of a hole and an electron may give rise to an exciton which may undergo radiative decay  
10       to the ground state by releasing a photon. In practice, the anode is commonly a mixed oxide of tin and indium for its conductivity and transparency. The mixed oxide (ITO) is deposited on a transparent substrate such as glass or plastic so that the light emitted by the organic film may be observed. The organic film may be the composite of several individual layers each designed for a distinct function. The individual layers  
15       of the organic film may be all polymeric in nature or combinations of films of polymers and films of small molecules deposited by thermal evaporation. The cathode is commonly a metallic film deposited on the surface of the organic film by either evaporation or sputtering.

          Although organic electroluminescent devices have shown promise as  
20       emissive displays, certain improvements in their performance are believed to be needed before they can become widely accepted. Chief among these needed improvements are lower drive voltage and higher efficiency, which are of particular importance for applications in hand-held, and portable electronics because of power supply considerations.

25           One approach to these needed improvements has been the incorporation of a conducting polymer film into electroluminescent devices, specifically in between ITO and a light emitting polymer. Yang and Heeger described (*Mol. Cryst. Liq. Cryst.*, Vol. 256, pp. 537-542, 1994, also WO 95/24056) improved device performance when a film of cresol-soluble conducting polyaniline (emeraldine salt) was inserted between ITO and MEH-PPV, the light-emitting polymer. The  
30       observed brightness at 6 volts was only 200 Cd/m<sup>2</sup>, however. A better result was obtained by Karg et al. (*Synthetic Metals*, Vol. 80, pp. 111-117, 1996) on MEH-PPV devices using a film of water-soluble conducting polyaniline (PanAquas™).

Brightness of 2000 Cd/m<sup>2</sup> at 5 volts represents a significant improvement, but the 1.2 lumens/watt efficiency is still rather low. Carter et al. (*Applied Physics Letters*, Vol. 70, pp. 2067-2069, 1997) compared the performance of MEH-PPV devices with water-soluble polyaniline and a water-soluble poly(3,4-ethylenedioxy-thiophene) (Baytron P<sup>TM</sup> from Bayer AG) and found them to be similar. Cao et al. in *Synthetic Metals*, Vol. 87, pp. 172-174, 1997 reported that a Baytron P<sup>TM</sup>/MEH-PPV device had brightness of 600 Cd/m<sup>2</sup> at 4 volts and 70 mA/cm<sup>2</sup>, corresponding to efficiency of 0.86 Cd/A and 0.67 lumen/watt. Carter et al. (*Applied Physics Letters*, Vol. 71, pp. 34-36, 1997) showed that Baytron P<sup>TM</sup> can be used in conjunction with PPV. Although some improvement was noted, device efficiency (0.75 to 0.90 lumen/watt) was still low. Thus, the above references have demonstrated that a conducting polymer film positioned between the anode and the electroluminescent layer can bring about a lowering of the drive voltage needed to attain a certain brightness but may not lead to significant increase in efficiency.

In one aspect, this invention is an electroluminescent device comprising a light-emitting organic film, arranged between an anode material and a cathode material such that under an applied voltage, the device is forward biased and holes are injected from the anode material into the organic film adjacent to the anode material and electrons are injected from the cathode material into the organic film adjacent to the cathode material, resulting in light emission from the light-emitting organic film; wherein the device additionally comprises a solution-processed film of a blend of an acid-functional non-conductive polymer and a conductive polymer positioned between the anode material and the light-emitting organic film, wherein the weight ratio of non-conducting polymer to conducting polymer is at least 0.75:1.

It has been discovered that the use of a blend of a soluble conducting polymer and a soluble non-conducting polymer surprisingly results in an increase in device efficiency, relative to devices which contain a layer of the water-soluble conducting polymer by itself. Since the acid-functional polymer is not electrically conductive and the preparation of a blend using such a non-conductive polymer effectively dilutes the concentration of the conducting polymer, this effect is considered surprising. These and other advantages of the invention will be apparent from the description which follows.

The term "solution-processed film" as used herein refers to a film prepared by depositing a water- or organic solvent-based solution of soluble material onto a first substrate, and then removing enough of the water or solvent to form a film  
5 of the material which is sufficiently stable to permit it to serve as a substrate for the deposition of additional film-forming liquid materials.

Suitable conductive polymers for use in preparing the device of the invention are polymers having an average molecular weight of greater than 1000 Daltons and which can be processed using solution processing techniques into a film  
10 having a thickness of less than 10,000 nm. Such polymers also have an electrical conductivity of at least  $10^{-6}$  Siemens/cm (S/cm), preferably at least  $10^{-4}$  S/cm, and most preferably at least  $10^{-2}$  S/cm. Examples of such include polyanilines, polythiophenes, and polypyrroles. Such polymers are typically "doped" to form an electronically-conductive complex of the protonated polymer which is more  
15 processible, conductive, or stable than the corresponding polymer in its un-doped form. A preferred method for preparing a water-soluble doped polymer is a template synthesis method as described, for example, in U.S. Patent 5,489,400 and in WO 97/03127. Such a method generally includes the steps of complexing the monomers used to prepare the conductive polymer with the long-chain dopant, and then adding  
20 an oxidant to the complex and polymerizing the complexed monomers to form the conductive polymer.

Suitable non-conductive polymers for use in the invention are polymers having an average molecular weight of greater than 1,000 Daltons, which can be processed using solution processing techniques into a film having a thickness of less  
25 than 10,000 nm. Such polymers have an electrical conductivity of less than  $10^{-10}$  S/cm and a pKa of less than 5, more preferably less than 3, and most preferably of less than 1. Examples of such include polymers having pendant groups selected from sulfonic acid, sulfinic acid, carboxylic acid, phosphoric acid, phosphonic acid, phosphinic acid, and  $-N+(R)^2H$  where R is selected from hydrogen,  $C_1$ - $C_{20}$  hydrocarbyl,  
30 hydroxy, alkoxy, and aryloxy. Specific examples of acid polymers include poly(styrenesulfonic acid) (PSS), poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (AMP), polyacrylic acid, polymethacrylic acid; all are available commercially. Other acid polymers useful in the invention are sulfonated polyphenylenes such as those

disclosed by Rulkens et al. in *Ber. Bunsenges. Phys. Chem.* Vol. 100, pp. 707-714, 1996 and by Rau and Rehahn in *Polymer Communications*, Vol. 34, pp. 2889-2893, 1993, and polyphenylenes bearing carboxylic acid functional groups such as the one reported by Chaturvedi et al. in *Macromolecules*, Vol. 26, pp. 2606-2611, 1993 and blends thereof.

The (a) non-conductive polymer and (b) conductive polymers are preferably utilized in an amount sufficient to provide a weight ratio of (a):(b) of at least 0.75:1, more preferably at least 1:1, and most preferably at least 1.5:1. If the conductive polymer is doped with a non-conductive polymeric acid, for the purposes of determining the weight ratios of non-conductive:conductive polymer, the non-conductive polymer amounts referred to above refer to polymers which are present in an excess amount, relative to the stoichiometric amount needed to dope the conductive polymer.

The devices of the invention may be prepared by any suitable method, but are preferably prepared by depositing relatively thin films of organic and inorganic materials onto a transparent substrate, starting with an anode material, optionally followed by one or more films of any additional organic or inorganic hole-transport materials, followed by one or more films of at least one electroluminescent polymer, optionally followed by any additional layers of organic or inorganic and electron-transport material(s) (in addition to the cathode material), which are then followed by depositing a layer of a cathode material. The layers of material may be prepared by any method suitable for the preparation of a thin film thereof, such as, for example, sputtering, spin-coating, or vapor deposition. Further, the particular technique employed to deposit a thin layer of organic material may require the use of a suitable organic solvent.

The term "anode material" as used herein refers to a semi-transparent or transparent conducting film with a work function between 4.5 eV and 5.5 eV. Examples of suitable anode materials include oxides and mixed oxides of indium and tin, and gold, but is preferably a mixed oxide of tin and indium ("ITO"). The metal oxide is deposited on a transparent substrate such as glass or a solvent-resistant transparent plastic material such as a polyester sheet, so that the light emitted by the EL organic film may be observed.

The organic film(s) within the device may be a multi-layer composite of several individual layers, each of which are designed for a distinct function, or may be one or more layers of a single material. Since holes are injected from the anode material, any organic film next to the anode material needs to have the functionality of transporting holes. Similarly, any layer next to the cathode material needs to have the functionality of transporting electrons. A layer of an electroluminescent organic material is also required. In some instances, a single organic material can perform the combined functions of hole and electron transport and light emission. The term "Electroluminescent organic film" as used herein refers to an organic film which, upon the injection of electrons and holes into it from opposite sides of the film, produce excitons which can relax to the ground state by emitting photons, preferably corresponding to wavelengths in the visible range. The term "organic film" as used herein means a film of an organic polymer, or a film of one or more organic molecules deposited by thermal evaporation or by solution processing. It is preferred that the total thickness of each organic film be less than 5000 nanometers (nm). It is more preferred that the thickness of the combined layers of organic film(s) be less than 5000 nm, and most preferably less than 3000 nm.

The ITO-coated glass which preferably serves as the anode and the substrate for depositing the organic film(s) thereon is preferably cleaned with detergent, organic solvents or UV-ozone treated prior to deposition of the organic film(s).

The term "hole-transporting organic film" as used herein refers to a layer of a film of a compound or polymer which, when disposed between two electrodes to which a field is applied and holes are injected from the anode, permits adequate transport of holes into the EL organic film. The term "electron-transporting organic film" as used herein refers to a layer of a film of a compound or polymer which, when disposed between two electrodes to which a field is applied and electrons are injected from the cathode, permits adequate transport of electrons into the electroluminescent organic film. If a separate hole-transport organic film and/or electron-transport film is used to prepare the electroluminescent device, such films may also have some degree of electroluminescence, but their electroluminescence efficiency will be less than that of the electroluminescent film.

The film of a blend of conductive and non-conductive polymers preferably serves as a hole-transport layer in the device of the invention. However, additional layers of other organic materials which have a hole-transport function may also be utilized as additional layers in the device. Hole-transporting polymers typically are comprised of triarylamine moieties. In cases where a separate organic layer selected for its hole-transport properties is utilized, the polymeric arylamines described in WO97/33193; U.S. Patent Application Serial No. 08/967,348 (allowed) filed on October 27, 1997; and U.S. Patent 5,728,801 may be used, all of which are hereby incorporated by reference. Other known hole-conducting polymers, such as polyvinylcarbazole, and semi-conducting polymers such as doped polyaniline, doped poly(3,4-ethylene-dioxythiophene), and doped polypyrrole may be used as additional hole-transport layers.

The resistance of this hole-transport layer(s) to erosion by the solution of the organic films which may be subsequently applied to the composite structure is obviously critical to the successful fabrication of multi-layer devices. Resistance to erosion may be increased by, for example, choosing a high molecular weight or crosslinkable hole-transport polymer, or by selecting a hole-transport polymer which is insoluble in the particular solvent used to deposit the electroluminescent polymer. The thickness of this hole-transport layer is preferably 500 nm or less, preferably 300 nm or less, most preferably 150 nm or less. In a preferred embodiment, layers of hole-transporting polymer films are arranged so that the layer closest to the anode has the lower oxidation potential, with the adjacent layers having progressively higher oxidation potentials. By these methods, electroluminescent devices having relatively high light output per unit voltage may be prepared.

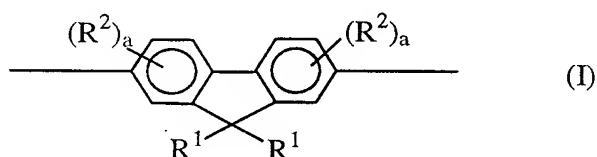
In the case where a separate electron-transporting organic layer is used, it may be applied either by thermal evaporation of low molecular weight materials or by solution coating of a polymer with a solvent that would not cause significant damage to the underlying electroluminescent organic film. Examples of low molecular weight materials include the metal complexes of 8-hydroxyquinoline (as described in Burrows et al., Applied Physics Letters, Vol. 64, pp. 2718-2720 (1994)), metallic complexes of 10-hydroxybenzo(h)quinoline (as described in Hammed et al., Chemistry Letters, pp. 905-906 (1993)), 1,3,4-oxadiazoles (as described in Hammed et al., Optoelectronics - Devices and Technologies, Vol. 7, pp. 83-93 (1992)), 1,3,4-



triazoles (as described in Kido et al., Chemistry Letters, pp. 47-48 (1996)), and dicarboximides of perylene (as described in Yoshida et al., Applied Physics Letters, Vol. 69, pp. 734-736 (1996)).

Polymeric electron-transporting materials useful in making electron-transporting organic films are exemplified by 1,3,4-oxadiazole-containing polymers (as described in Li et al., Journal of Chemical Society, pp. 2211-2212 (1995), and in Yang and Pei, Journal of Applied Physics, Vol. 77, pp. 4807-4809 (1995)), 1,3,4-triazole-containing polymers (as described in Strukelj et al., Science, Vol. 267, pp. 1969-1972 (1995)), quinoxaline-containing polymers (as described in Yamamoto et al., Japan Journal of Applied Physics, Vol. 33, pp. L250-L253 (1994), and in O'Brien et al., Synthetic Metals, Vol. 76, pp. 105-108 (1996)), cyano-PPV (as described in Weaver et al., Thin Solid Films, Vol. 273, pp. 39-47 (1996)), and fluorene-containing polymers, as described, for example, in U.S. Patent 5,708,130 and in U.S. Patent Application Serial No. 08/861,469, filed on May 21, 1997. The thickness of this layer may be 500 nm or less, preferably 300 nm or less, most preferably 150 nm or less.

In a preferred embodiment, the electroluminescent organic film is a film containing at least one fluorene based polymer. Preferably, the fluorene based polymer comprises monomeric units of the formula:

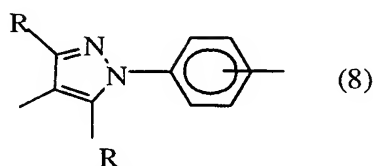
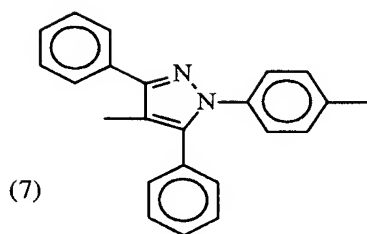
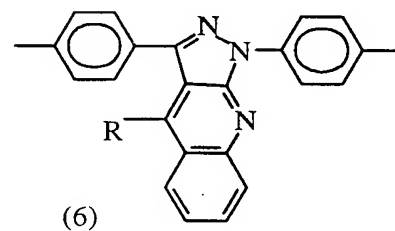
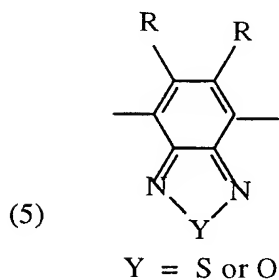
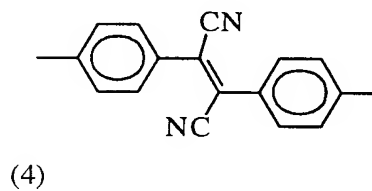
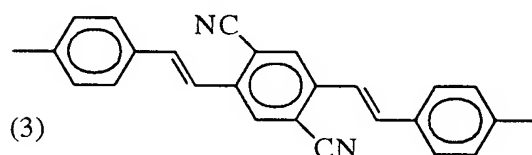
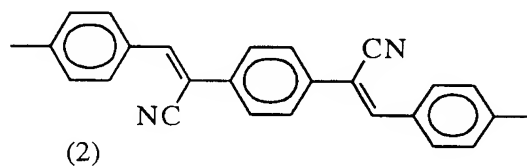
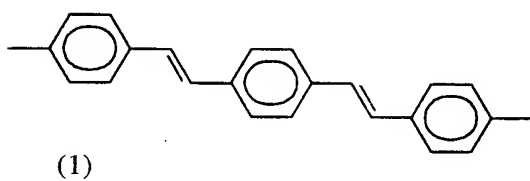


wherein R¹ is independently in each occurrence H, C<sub>1-20</sub> hydrocarbyl or C<sub>1-20</sub> hydrocarbyl containing one or more S, N, O, P or Si atoms, C<sub>4-16</sub> hydrocarbyl carbonyloxy, C<sub>4-16</sub> aryl(trialkylsiloxy) or both R¹ may form with the 9-carbon on the fluorene ring a C<sub>5-20</sub> cycloaliphatic structure or a C<sub>4-20</sub> cycloaliphatic structure containing one or more heteroatoms of S, N or O;

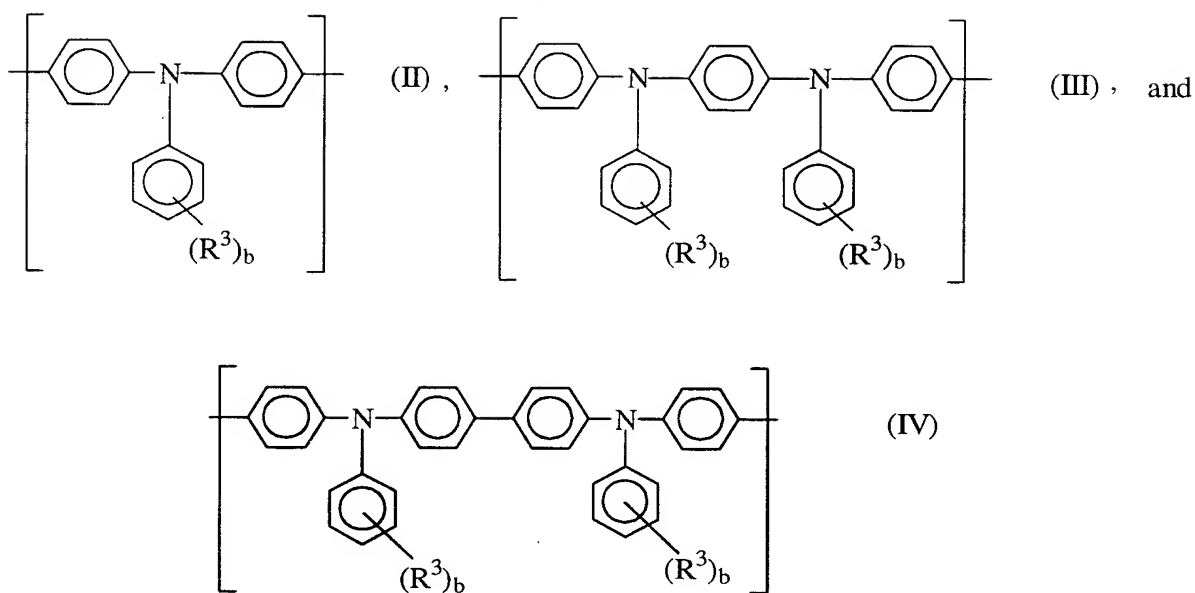
R² is independently in each occurrence C<sub>1-20</sub> hydrocarbyl, C<sub>1-20</sub> hydrocarbyloxy, C<sub>1-20</sub> thioether, C<sub>1-20</sub> hydrocarbylcarbonyloxy or cyano; and

a is independently in each occurrence a number of from 0 to 3. The fluorene monomeric unit preferably occurs at least 10 times and no more than 10,000 times in the polymer. In the above formula, R¹ is preferably in each occurrence n-octyl.

The preferred polymer may be a homopolymer of fluorene or may be a copolymer of the fluorene monomeric unit with an additional monomeric unit such as

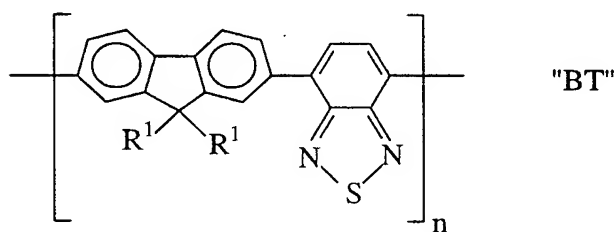


wherein R is a hydrocarbyl having 1-20 carbon atoms, e.g., methyl, ethyl, isopropyl, n-hexyl, n-octyl, phenyl, benzyl, and naphthyl, optionally further substituted by substituents containing heteroatoms such as oxygen, nitrogen, and sulfur.



- 5 wherein  $R^3$  is independently in each occurrence carboxyl,  $C_1$ - $C_{20}$  alkyl,  $C_1$ - $C_{20}$  alkoxy or a group of the formula  $-CO_2R^4$  wherein  $R^4$  is a  $C_1$ - $C_{20}$  alkyl; and  
 b is independently in each occurrence an integer from 0 to 3.

If a copolymer is used, the monomeric units are preferably alternating.  
 Blends of the polymers are especially preferred, such as a blend of a homopolymer of  
 10 the monomer of formula 1 with from 0.1 to 50 percent by weight of an alternating  
 copolymer of monomers of formula 1 with the comonomers listed above. A preferred  
 example of such copolymers has the formula:



wherein  $R^1$  is as defined for formula 1 and  $n$  is an integer greater than 10 and less than 10,000. The BT polymer is preferably used in an amount, based on the weight of the polymers in the blend, of at least 1 percent, more preferably at least about 3 percent; but preferably no greater than 20 percent, more preferably no greater than 10 percent, and most preferably no greater than 5 percent.

The term "cathode material" as used herein refers to a conducting metal film with a work function between 2.5 eV and 4.5 eV. In the device of the first aspect of the invention, the cathode material comprises calcium. The cathode of calcium may be deposited by any suitable technique, such as thermal evaporation or by sputtering. The thickness of the cathode is preferably from 1 nm to 10,000 nm. If desired, the film of calcium may be coated with another film of a metal having a higher work function, such as aluminum or silver, to improve stability. The thickness of the additional layer is preferably at least 100 nm, more preferably at least 250 nm, most preferably at least 500 nm; but preferably no greater than 10,000 nm, more preferably no greater than 5,000 nm, and most preferably no greater than 1,000 nm. Among all metals which form the organic/metal interface between the organic material(s) and the metal cathode, calcium preferably comprises at least 20 percent of the thickness of such film, more preferably at least 50 percent, and most preferably 100 percent.

The devices of this invention preferably emit light having a brightness of at least 100 Cd/m<sup>2</sup> when subjected to an applied voltage of no more than 50 volts, preferably no more than 10 volts, and most preferably no more than 5 volts.

#### Example 1

Electroluminescent devices are prepared by depositing a water-based blend as described in Table 1 onto indium-tin-oxide-coated glass and allowing the film to dry. The conducting polymer is doped poly(3,4-ethylenedioxythiophene, purchased as 1.3 weight percent aqueous dispersion of poly(3,4-ethylenedioxythiophene) and poly(styrenesulfonic acid) in a weight ratio of 1:16 or mole ratio of 1:1.2 (as Baytron P<sup>TM</sup> from Bayer). The excess acid polymers used are poly(styrenesulfonic acid) (PSS) obtained from Scientific Polymer Products, Inc. and poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (AMP) from Aldrich Chemicals. These films are dried at 200°C in air for 5 minutes. The resulting films have the thicknesses specified in Table 1. An electroluminescent film of a polymer blend (5 weight percent of BT and

95 weight percent of F8; having a thickness of about 150 nm, is then prepared on top of the film containing poly(3,4-ethylenedioxythiophene). Cathodes are then deposited on the electroluminescent layer using a vapor deposition technique from calcium (approximately 150 nm) with a silver overcoat (approximately 160 nm) using a vapor  
5 deposition technique.

The resulting devices are tested and the data is shown in Table 1. Each device is characterized by the voltage and current required to reach brightness of 200 Cd/m<sup>2</sup> and 4000 Cd/m<sup>2</sup>. Device efficiency is expressed as Cd/A and lumens/watt (Lu/W). The former values are obtained by dividing brightness (Cd/m<sup>2</sup>)  
10 by the emitting area, and the latter values are calculated from the formula  $\text{Lu/W} = \pi (\text{Cd/A})/V$  where V is the voltage at the specified brightness and Cd/A is the efficiency at the same brightness. The values presented in Table 1 are average values of 8-10 devices.

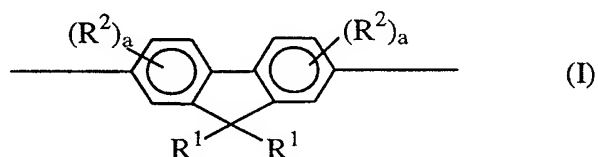
Ex. No.	No. of Devices	Polymer	Baytron P <sup>TM</sup> /Polymer		200 Cd/m <sup>2</sup>			4000 Cd/m <sup>2</sup>		
			Ratio <sup>b</sup>	Thickness <sub>s</sub> (nm)	Volts	Lu/W	Cd/A	Volts	Lu/W	Cd/A
1A	8	none	1:0	100	6.2	0.3	0.6	11.9	0.4	1.3
1B	10 <sup>a</sup>	none	1:0	70	6.9	0.7	1.6	13.0	0.7	2.7
1C	9	none	1:0	70	7.4	1.1	2.3	15.0	0.6	2.7
1D	9	PSS	1:1	70	3.7	2.4	2.8	9.6	0.9	2.6
1E	9	PSS	1:1	100	3.3	3.4	3.5	6.8	1.7	3.7
1F	9	PSS	1:1.5	100	3.1	3.5	3.5	5.9	2.2	4.2
1G	8	PSS	1:2	70	3.2	3.4	3.4	6.3	1.5	3.0
1H	9	PSS	1:2	100	3.1	4.9	4.8	5.7	2.5	4.5
1K	9	PSS	1:2.5	100	3.1	5.1	5.1	5.8	2.4	4.3
1M	9	PSS	1:3	100	3.2	4.4	4.6	7.3	1.5	3.4
1N	9	PSS	1:4	100	3.3	1.5	1.5	6.3	1.1	2.0
1P	9	AMP	1:2	100	4.6	1.8	2.5	9.5	1.6	4.4

<sup>a</sup> Baytron P<sup>TM</sup> /PSS films dried at 120°C for 3 hours.

<sup>b</sup> Ratio refers to the weight ratio of Baytron P<sup>TM</sup> to the second polymer which is PSS or AMP.

CLAIMS:

1. An electroluminescent device comprising a light-emitting organic film, arranged between an anode material and a cathode material such that under an applied voltage, the device is forward biased and holes are injected from the anode material into the organic film adjacent to the anode material and electrons are injected from the cathode material into the organic film adjacent to the cathode material, resulting in light emission from the light-emitting organic film; wherein the device additionally comprises a solution-processed film of a blend of an acid-functional non-conductive polymer and a conductive polymer positioned between the anode material and the light-emitting organic film, wherein the weight ratio of non-conducting polymer to conducting polymer is at least 0.75:1.
2. The device of Claim 1 wherein the conductive polymer has a conductivity of at least  $10^{-4}$  S/cm.
3. The device of Claim 1 wherein the conductive polymer is a conductive polyaniline, polythiophene, polypyrrole, or a mixture thereof.
4. The device of Claim 1 wherein the non-conductive polymer has a pKa of less than 3.
5. The device of Claim 1 wherein the non-conductive polymer is poly(styrenesulfonic acid), poly(2-acrylamido-2-methyl-1-propanesulfonic acid), polyacrylic acid, polymethacrylic acid, or a mixture thereof.
6. The device of Claim 1 wherein the electroluminescent organic film is a film containing a polyfluorene.
7. The device of claim 1 wherein the organic film contains a fluorene based polymer comprising monomeric units of the formula:



wherein  $R^1$  is independently in each occurrence H,  $C_{1-20}$  hydrocarbyl or  $C_{1-20}$  hydrocarbyl containing one or more S, N, O, P or Si atoms,  $C_{4-16}$  hydrocarbyl carbonyloxy,  $C_{4-16}$  aryl(trialkylsiloxy) or both  $R^1$  may form with the 9-carbon on the

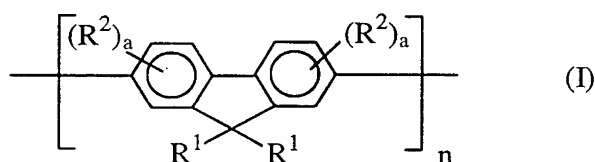
fluorene ring a C<sub>5-20</sub> cycloaliphatic structure or a C<sub>4-20</sub> cycloaliphatic structure containing one or more heteroatoms of S, N or O;

R<sup>2</sup> is independently in each occurrence C<sub>1-20</sub> hydrocarbyl, C<sub>1-20</sub> hydrocarbyloxy, C<sub>1-20</sub> thioether, C<sub>1-20</sub> hydrocarbylcarbonyloxy or cyano; and

5 a is independently in each occurrence a number of from 0 to 3.

8. The device of claim 6 wherein the film also contains at least one fluorene containing copolymer.

9. The device of Claim 1 wherein the electroluminescent organic film comprises at least fifty percent by weight of a polyfluorene of the formula:



10

wherein R<sup>1</sup> is independently in each occurrence H, C<sub>1-20</sub> hydrocarbyl or C<sub>1-20</sub> hydrocarbyl containing one or more S, N, O, P or Si atoms, C<sub>4-16</sub> hydrocarbyl carbonyloxy, C<sub>4-16</sub> aryl(trialkylsiloxy) or both R<sup>1</sup> may form with the 9-carbon on the fluorene ring a C<sub>5-20</sub> cycloaliphatic structure or a C<sub>4-20</sub> cycloaliphatic structure containing one or more heteroatoms of S, N or O;

15

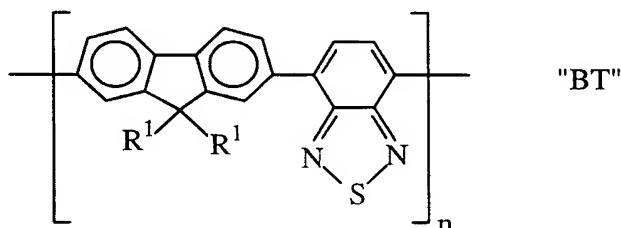
R<sup>2</sup> is independently in each occurrence C<sub>1-20</sub> hydrocarbyl, C<sub>1-20</sub> hydrocarbyloxy, C<sub>1-20</sub> thioether, C<sub>1-20</sub> hydrocarbylcarbonyloxy or cyano;

a is independently in each occurrence a number of from 0 to 3; and

n is a number greater than 10.

20

10. The device of Claim 9 wherein the electroluminescent film additionally comprises from 0.1 to 50 percent by weight of a polymer of the formula:





wherein R1 is independently in each occurrence H, C<sub>1-20</sub> hydrocarbyl or C<sub>1-20</sub> hydrocarbyl containing one or more S, N, O, P or Si atoms, C<sub>4-16</sub> hydrocarbyl carbonyloxy, C<sub>4-16</sub> aryl(trialkylsiloxy) or both R' may form with the 9-carbon on the fluorene ring a C<sub>5-20</sub> cycloaliphatic structure or a C<sub>4-20</sub> cycloaliphatic structure  
5 containing one or more heteroatoms of S, N or O; and n is an integer greater than 10.

11. The device of any of the preceding claims which emits light having a brightness of at least 100 Cd/m<sup>2</sup> when subjected to an applied voltage of 50 volts.

12. The device of any of claims 1-10 which emits light having a  
10 brightness of at least 100 Cd/m<sup>2</sup> when subjected to an applied voltage of 5 volts.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/16834

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09K11/06 H05B33/14 H01B1/12

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09K H05B H01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 05187 A (PICHLER KARL ;TOWNS CARL (GB); CAMBRIDGE DISPLAY TECH (GB)) 5 February 1998 (1998-02-05) embodiment III page 12, paragraph 1 ---	1-5, 11, 12
X	US 5 777 070 A (INBASEKARAN MICHAEL ET AL) 7 July 1998 (1998-07-07) column 6, line 60 -column 8, line 61; example 2 --- -/--	1-12

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

26 October 1999

Date of mailing of the international search report

03/11/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Shade, M

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/16834

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>CARTER S A ET AL: "Polymeric anodes for improved polymer light-emitting diode performance"</p> <p>APPLIED PHYSICS LETTERS, vol. 70, no. 16, 21 April 1997 (1997-04-21), pages 2067-2069 2069, XP002110222 ISSN: 0003-6951 cited in the application table 1</p> <p style="text-align: center;">---</p>	1-5, 11, 12
E	<p>EP 0 949 850 A (CAMBRIDGE DISPLAY TECH) 13 October 1999 (1999-10-13) column 7, line 10 - line 49</p> <p style="text-align: center;">---</p>	1-12
A	<p>WO 97 33323 A (UNIAX CORP) 12 September 1997 (1997-09-12) example 20</p> <p style="text-align: center;">---</p>	1-12
A	<p>EP 0 813 212 A (NIPPON CATALYTIC CHEM IND) 17 December 1997 (1997-12-17) example 7</p> <p style="text-align: center;">---</p>	1-5, 11, 12
A	<p>WO 97 32452 A (UNIAX CORP) 4 September 1997 (1997-09-04) page 13, line 8 - line 34</p> <p style="text-align: center;">-----</p>	1-5, 11, 12

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/16834

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9805187 A	05-02-1998	EP 0915925 A EP 0947123 A WO 9804610 A GB 2331400 A	19-05-1999 06-10-1999 05-02-1998 19-05-1999
US 5777070 A	07-07-1998	WO 9920675 A	29-04-1999
EP 0949850 A	13-10-1999	GB 2335884 A	06-10-1999
WO 9733323 A	12-09-1997	EP 0885461 A US 5900327 A	23-12-1998 04-05-1999
EP 0813212 A	17-12-1997	JP 10060108 A JP 10279798 A	03-03-1998 20-10-1998
WO 9732452 A	04-09-1997	US 5798170 A AU 2192197 A	25-08-1998 16-09-1997